## **Electronic Supplementary Information**

## Turn-on Fluorescence Response Upon Anion Binding to Dimesitylboryl-Functionalized Quaterthiophene

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**Materials and Methods.** Tetrabutylammonium rhodanide and tetrabutylammonium fluoride (TBAF, 1.0 M in THF) were purchased from Aldrich, tetrabutylammonium bromide, tetrabutylammonium nitrate, KF, and 18-crown-6 from Fisher Scientific, tetrabutylammonium chloride from Fluka, tetrabutylammonium iodide from MP Biomedical LLC, and tetrabutylammonium azide from TCI. All reactions and manipulations were carried out under an atmosphere of pre-purified nitrogen in an inert atmosphere glove box (mBraun). Ether solvents were distilled from Na / benzophenone prior to use. Hydrocarbon and chlorinated solvents were purified using a solvent purification system (Innovative Technologies, alumina / copper columns for hydrocarbon solvents), and chlorinated solvents were subsequently distilled from CaH<sub>2</sub> and degassed via several freeze-pump-thaw cycles.

The 499.9 MHz <sup>1</sup>H, 125.7 MHz <sup>13</sup>C, and 160.4 MHz <sup>11</sup>B NMR spectra were recorded on a Varian INOVA 500 MHz spectrometer with a boron-free probe using quartz NMR tubes. The <sup>1</sup>H and <sup>13</sup>C NMR spectra were referenced internally to the solvent peaks and the <sup>11</sup>B NMR spectra externally to BF<sub>3</sub>•Et<sub>2</sub>O ( $\delta = 0$ ) in C<sub>6</sub>D<sub>6</sub>. UV-vis absorption data were acquired on a Varian Cary 500 UV-Vis / NIR spectrophotometer. The fluorescence data and quantum yields were measured on a Varian Cary Eclipse fluorescence spectrophotometer with optically dilute solutions (A<0.1). Anthracene was used as the standard for determination of the quantum yields ( $\Phi = 0.33$ ). Sample solutions were prepared using a microbalance (±0.1 mg) and volumetric glassware. The quantum yields were calculated by plotting a graph of integrated fluorescence intensity *vs* absorbance of at least four solutions with increasing concentration. The gradient of the graph is proportional to the quantum yield. The quantum yields were corrected for different solvent refractive indices according to the following formula, where  $\eta$  is the refractive index of the solvent.

 $\Phi = \Phi_{standard} \times [Gradient_{compound} \times (\eta_{compound})^2] / [Gradient_{standard} \times (\eta_{standard})^2]$ For titration experiments, fluoride and cyanide ion solutions were prepared by diluting the TBAF solution (1.0 M in THF) and dissolving tetrabutylammonium cyanide to the desired concentration; stock solutions of the samples were prepared in THF in the glove box. Fluoride and cyanide were added to the sample solution under investigation through a microsyringe (±0.1 µL) under nitrogen in a glove box. Binding constants were determined using the program Hyperquad<sup>TM</sup>. For the fluoride binding simulation, data at 14 different wavelengths were chosen from 500 to 290 nm; for the cyanide binding simulation, data at 16 different wavelengths were used from 480 to 290 nm (every 10 nm with omission of wavelengths close to isosbestic points).

High-resolution mass spectral data for the complexes were obtained on an Apex-ultra 7 Hybrid FT-MS (Bruker Daltonics) using electrospray ionization. Elemental analyses were obtained from Quantitative Technologies Inc., Whitehouse, NJ. Single crystal X-ray diffraction intensities were collected on a Smart Apex2 CCD diffractometer at 100 K using Cu K $\alpha$  (1.54178 Å) radiation and deötails of the X-ray diffraction experiments and crystal structure refinements are given in Table S1. The structures were solved by direct methods and refined by full-matrix least squares based on  $F^2$  with all reflections (SHELXTL V5.10; G. Sheldrick, Siemens XRD, Madison, WI). Non-hydrogen atoms were refined with anisotropic displacement coefficients, and hydrogen atoms were treated as idealized contribution. SADABS (Sheldrick, G.M.; SADABS, 2008, University of Göttingen) absorption correction was applied. Crystallographic data for the structures of **QTB-CN** and **QTB-F** have been deposited with the Cambridge Crystallographic Data Center as supplementary publications CCDC-828004 and 828005, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; email: deposit@ccdc.cam.ac.uk).

DFT (B3LYP, 6-31G(d)) calculations were performed with the Gaussian03 program. Geometries for **QTB-F** and **QTB-CN** were obtained from the single crystal X-ray data. All other input files and the orbital representations were generated with Gaussview 3.0.7. Orbital energies and excitation data were calculated using TD-DFT (B3LYP, 6-31G(d)).

**Synthesis of complex QTB-F.** A solution of **QTB** (50 mg, 0.059 mmol) in 5 mL of THF was slowly added to a mixture of KF (30 mg, 0.51 mmol) and 18-crown-6 (34.0 mg, 0.129 mmol) in THF while stirring. The reaction mixture was stirred at RT for 12 h followed by the removal of the solvent. The residue was washed with 2×10 mL of hexanes and then with 2 mL of dry ether. Clear yellow-orange crystals were obtained by layering a THF solution of the crude product with hexanes. Yield: 42 mg (48%). For **QTB-F**: <sup>1</sup>H NMR (CD<sub>3</sub>CN, 499.9 MHz):  $\delta = 6.58$  (s, 8H, Mes), 6.51 (br, 2H, Th), 6.40 (br, 2H, Th), 6.25 (br, 2H, Th), 3.55 (s, 48H, 18-c-6), 2.36 (s, 12H, *p*-Me), 2.19 (s, 24H, *o*-Me), 1.96 (s, 6H, Me); <sup>13</sup>C NMR (CD<sub>3</sub>CN, 125.7 MHz): 155.9, 142.5, 140.8, 137.1, 135.6, 135.5, 133.8, 133.1, 132.5, 129.2, 126.3, 126.2, 71.0, 24.8, 21.1, 15.3; <sup>11</sup>B NMR (CD<sub>3</sub>CN, 160.3 MHz):  $\delta = 4.7$  (w<sub>1/2</sub> = 960 Hz). High res MS for complex with Bu<sub>4</sub>N<sup>+</sup> counterions: (electrospray, (-) mode): m/z 1134.6212 ([M–Bu<sub>4</sub>N]<sup>-</sup>, 100%, calcd for <sup>12</sup>C<sub>70</sub> H<sub>92</sub><sup>11</sup>B<sub>2</sub><sup>19</sup>F<sub>2</sub><sup>14</sup>N<sub>1</sub><sup>32</sup>S<sub>4</sub>1134.6267), 378.2842 ([M–Bu<sub>4</sub>N]<sup>3-</sup>, 5%, calcd 378.2089).

**Synthesis of complex QTB-CN.** A solution of **QTB** (50 mg, 0.059 mmol) in 5 mL of THF was slowly added to a solution of ["Bu<sub>4</sub>N]CN (30 mg, 0.51 mmol) in THF while stirring. The reaction mixture was stirred at RT for 12 h followed by the removal of the solvent. The residue was washed with 2×10 mL of hexanes and then with 2 mL of dry ether. Clear yellow-orange crystals were obtained by layering a CH<sub>2</sub>Cl<sub>2</sub> solution of the crude product with hexanes. Yield: 47 mg (58%). For **QTB-CN**: <sup>1</sup>H NMR (CD<sub>3</sub>CN, 499.9 MHz):  $\delta = 6.58$  (s, 8H, Mes), 6.51 (br, 2H, Th), 6.40 (br, 2H, Th), 6.25 (br, 2H, Th), 3.07 (m, 16H, CH<sub>2</sub>), 2.36 (s, 12H, *p*-Me), 2.19 (s, 24H, *o*-Me), 2.14 (s, 6H, Me), 1.59 (m, 16H, CH<sub>2</sub>), 1.35 (m, 16H, CH<sub>2</sub>), 0.96 (m, 24H, CH<sub>3</sub>); <sup>13</sup>C NMR (CD<sub>3</sub>CN, 125.7 MHz): 143.1, 139.3, 138.0, 136.4, 134.1, 133.9, 133.3, 129.8, 127.7, 126.4, 59.4, 25.3, 24.4, 21.0, 20.4, 15.3, 13.9, not observed B-C; <sup>11</sup>B NMR (CDCl<sub>3</sub>, 160.3 MHz):  $\delta = -16$  (w<sub>1/2</sub> = 160 Hz). High res MS (electrospray, (-) mode): m/z 1148.6298 ([M–Bu<sub>4</sub>N]<sup>-</sup>, 100%, calcd for <sup>12</sup>C<sub>72</sub><sup>1</sup>H<sub>92</sub><sup>11</sup>B<sub>2</sub><sup>14</sup>N<sub>3</sub><sup>32</sup>S<sub>4</sub> 1148.6360), 382.9480 ([M–Bu<sub>4</sub>N]<sup>3-</sup>, 5%, calcd 382.8787). Analysis calcd for C<sub>88</sub>H<sub>128</sub>B<sub>2</sub>N<sub>4</sub>S<sub>4</sub>: C 75.94, H 9.27, N 4.03%; found C 75.25, H 9.58, N 4.35%.

**Complete Reference 15:** Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A. Gaussian 03, Revision C.02, Gaussian, Inc., Wallingford CT, 2004.

	QTB-F	QTB-CN
Empirical formula	$C_{94}H_{136}B_2F_2K_2O_{16}S_4 \qquad C_{88}H_{128}B_2N_4S_4$	
$M_r$	1788.09	1391.80
Т, К	100(2)	100(2)
Wavelength, Å	1.54178	1.54178
Crystal system	Triclinic	Triclinic
Space group	P -1	P-1
<i>a</i> , Å	10.7612(1)	11.6855(3)
b, Å	11.4101(2)	12.0398(3)
<i>c</i> , Å	21.9383(3)	16.0851(5)
a, °	89.5585(9)	78.460(2)
$\beta$ , °	88.1985(8)	74.957(2)
γ, °	63.2907(7)	70.046(2)
$V, Å^3$	2405.04(6)	2038.73(10)
Ζ	1	1
$\rho_{\rm calc},  {\rm g/cm^{-3}}$	1.235	1.134
$\mu$ (CuK $\alpha$ ),mm <sup>-1</sup>	2.210	1.405
F(000)	958	758
Crystal size, mm <sup>3</sup>	0.33 x 0.28 x 0.17	0.47 x 0.19 x 0.17
$\theta$ range, °	4.03 to 71.03	3.94 to 66.95
Index ranges	-12<=h<=12	-13<=h<=13
	-13<=k<=13	-14<=k<=13
	-25<=l<=25	-18<=1<=16
Reflections collected	23466	16583
Independent reflections	8064 [R(int) = 0.027]	6548 [R(int) = 0.0300]
Absorption correction	Numerical	Numerical
Refinement method	Full-matrix least-squares on $F^2$	Full-matrix least-squares on $F^2$
Data/restraints/ parameters	8064 / 0 / 569	6548 / 0 / 453
Goodness-of-fit on $F^2$	1.02	1.05
Final R indices $[I>2\sigma(I)]^a$	R1 = 0.043, wR2 = 0.106	R1 = 0.044, wR2 = 0.111
R indices (all data) <sup>a</sup>	R1 = 0.054, wR2 = 0.113	R1 = 0.053, wR2 = 0.118
Peak and hole (eÅ <sup>-3</sup> )	0.69 and -0.41	0.34 and -0.28

Table S1. Crystal data and structure refinement for QTB-F and QTB-CN

 $\overline{{}^{a} R_{1} = \Sigma ||F_{o}| - |F_{c}|| / |F_{o}|, wR_{2} = [\Sigma w (F_{o}^{2} - F_{c}^{2})^{2} / \Sigma w (F_{o}^{2})^{2}]^{1/2}}.$ 

	QTB-F	QTB-CN	QTB <sup>[b]</sup>
C22-C23	1.458(3)	1.461(3)	1.456 (2)
C19-C19A	1.448(4)	1.448(4)	1.450(3)
B-CN or F	1.462(3)	1.636(3)	N/A
B-C1	1.659(3)	1.679(3)	1.576(3)
B-C10	1.672(3)	1.667(3)	1.572(3)
B-C21	1.653(3)	1.662 (3)	1.576(2)
C10-B-C21	116.49(17)	109.25(15)	120.94(16)
C10-B-C1	115.48(17)	110.66(14)	122.84(15)
C1-B-C21	107.22(17)	119.15(15)	116.18(15)
Th <sup>B</sup> // Th <sup>B</sup>	0	0	0
$\mathrm{Th}^{\mathrm{B}}$ // $\mathrm{Th}^{\mathrm{Me}}$	16.0	31.0	15.2
$Th^{B} // Mes (c)$	83.7	78.6	79.6
$Th^{B} // Mes (t)$	67.1	59.4	70.19
Mes // Mes	83.9	85.4	84.3

Table S2. Selected Geometric Parameters (°, Å) of QTB-F and QTB-CN<sup>[a]</sup>

[a] Mes = mesityl ring,  $Th^B$  = boron-substituted thiophene ring,  $Th^{Me}$  = methyl-substituted thiophene ring, Mes (c) = Mes group facing central thiophene ring, Mes (t) = Mes group facing terminal thiophene ring.

[b] H. Li, A. Sundararaman, K. Venkatasubbaiah, F. Jäkle, J. Am. Chem. Soc. 2007, 129, 5792.

**Figure S1.** Plots of the X-ray structures of **QTB-F** and **QTB-CN** with atom labels (ellipsoids are drawn at the 50% probability level).





**Figure S2.** Calculated structures of **QTB-CN'** ((left side, conformation identical to that of **QTB-F** except for that the fluorides were replaced by cyanides) and **QTB-F'** (right side, conformation identical to that of **QTB-CN** except for that the cyanide anions were replaced by fluorides). All hydrogen atoms are omitted for clarity.



## Figure S3. Computed orbital plots (DFT, B3LYP, 6-31G(d))



Compound	HOMO (eV)	LUMO (eV)	HOMO-LUMO gap (eV)
QTB-F	-0.26	-2.89	2.63
QTB-CN	0.00	-2.77	2.77
QTB-F'	-0.21	-2.94	2.73
QTB-CN'	-0.07	-2.74	2.67
QT(F)	-1.42	-4.19	2.77
QT(CN)	-1.35	-4.23	2.88

**Table S3.** Calculated orbital energies (DFT, B3LYP, 6-31G(d))

Table S4. Calculated excitation energies (TD-DFT, B3LYP, 6-31G(d))

Compound		TD-DFT Results
QTB-F	$\lambda$ / nm; oscillator strength	447 (2.7744 eV); 1.0330
	Transition	237→238 (HOMO→LUMO), 0.63692
QTB-CN	$\lambda$ / nm; oscillator strength	429 (2.8901 eV); 0.9491
	Transition	241→242 (HOMO→LUMO), 0.64233
QTB-F'	$\lambda$ / nm; oscillator strength	433 (2.8630 eV); 0.9650
	Transition	237→238 (HOMO→LUMO), 0.64163
QTB-CN'	$\lambda$ / nm; oscillator strength	441 (2.8092 eV); 1.0175
	Transition	241→242 (HOMO→LUMO), 0.63896
QT(F)	$\lambda$ / nm; oscillator strength	423 (2.9316 eV); 1.1688
	Transition	93 <b>→</b> 94 (HOMO→LUMO), 0.63802
QT(CN)	$\lambda$ / nm; oscillator strength	406 (3.0540 eV); 1.0766
	Transition	93 <b>→</b> 94 (HOMO→LUMO), 0.64321

Figure S4. Absorption and emission spectra for QTB complexed with one and two equiv  $F^-$ , respectively, in THF.



**Figure S5.** Titration fits at selected wavelengths for complexation of **QTB** with a)  $F^-$  and b)  $CN^-$ . The blue diamonds correspond to experimental data points, the dashed red line to the fit; the solid red, blue and brown lines correspond to the relative concentrations of free acid, 1:1 complex and 1:2 complex at each given titration point.



b)



**Figure S6.** Absorption and emission spectra of **QTB** after exposure to an excess of  $F^-$  and  $CN^-$  (10 equiv each, added as a mixture in THF).

